

Dynamic Inhomogeneities in the La_2CuO_4 -Based Superconductors

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Polarization-dependent X-ray-absorption fine-structure (XAFS) measurements on the local structure of the La_2CuO_4 -based high- T_c superconductors $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, and $\text{La}_{1.6-x}\text{Sr}_x\text{Nd}_{0.4}\text{CuO}_4$ find, among others, orientation disorder induced in the $\text{Cu}-\text{O}_2$ planes by doping Sr, Ba, and alloying Nd atoms, all such atoms residing in La-sites. The orientation disorder is of two types: mostly static-buckling disorder, and dynamic disordering of the tilt angles of the $\text{Cu}-\text{O}_6$ octahedra correlated in nanoscale regions, with respect to neighboring nanoscale regions. Buckling disorder in the $\text{Cu}-\text{O}_2$ planes has the greatest detrimental effect on T_c and conductivity for such foreign atoms.

KEY WORDS: La_2CuO_4 -based superconductors; dynamic inhomogeneities; orientation disorder; high- T_c .

1. INTRODUCTION

It is generally recognized that knowledge of the structure of materials is fundamental to an understanding of their properties. The canonical method of determining this for crystalline materials is diffraction. However, structure determined by diffraction that neglects diffuse scattering measures the *average* periodic structure, and cannot detect nanostructure regions that are disordered with respect to each other, and, thus, will not correspond to the actual structure on the local interatomic scale [1]. The local structure has a special importance for the high- T_c superconductors because of their short superconducting (SC) coherence length of ≈ 10 – 20 Å. The pairing mechanism of SC is determined by interactions between atoms in the volume of the dimensions of the coherence length. If the local structure has a correlation length larger than the coherence length, then its structure is the relevant one for understanding the pairing mechanism, and not the average periodic structure as measured by diffraction. We have found local-disordered

nanostructure regions in the La_2CuO_4 high- T_c superconductors substituted with Sr, Ba, Ni, and Nd atoms [2–9]. In this paper we concentrate on orientation disorder induced by foreign atoms substituted in the La sites, yet produce effects in the $\text{Cu}-\text{O}_2$ planes, since some of these appear to be dynamic. Thus, Ni is not discussed since it substitutes in the $\text{Cu}-\text{O}_2$ planes. These structural deviations from the average periodic diffraction structure are in addition to much smaller strains induced by dynamic stripes which have been proposed as one mechanism of high- T_c SC.

Presently there is no consensus of the physical mechanism or mechanisms leading to SC in the copper-oxide materials. The La_2CuO_4 -based high- T_c materials are the simplest of the $\text{Cu}-\text{O}_2$ oxides with a single $\text{Cu}-\text{O}_2$ plane between two La–O planes. The usual approach to understanding the pairing mechanism of the high- T_c superconductors is to idealize their structures as simple periodic ones and assume that doping does not distort the structure but only adds carriers. In this paper we describe the orientation deviations from periodicity found in La_2CuO_4 -based high- T_c materials and some speculations on how they may affect the pairing mechanism.

Section 2 describes in more detail the distinction between the average periodic structure and the local

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structure. Section 3 follows describing the deviations from periodicity found in La_2CuO_4 high- T_c superconductors with added Sr, Ba, and Nd atoms. A discussion and summary are given in Section 4.

2. LOCAL STRUCTURE

To obtain the local deviations from the average periodic structure, the standard Bragg diffraction method needs to be supplemented. If any such local disorder is present in the crystal, the standard Bragg diffraction method is able to detect this only as a decrease in intensity in the Bragg peaks, since such disorder diverts some scattering into angles between the Bragg peaks, the diffuse scattering. Such a decrease in intensity would be interpreted only as a larger "thermal factor" of the vibration of atoms about their lattice sites. Detecting the local disorder requires including in the analysis the diffuse scattering between the Bragg peaks. An analysis of both the diffuse scattering and the Bragg peaks leads directly to the local structure [10] in the form of the pair distribution function (PDF). When there is more than one type of atom in the sample then the PDF is a sum of the partial PDFs (PPDFs), consisting of the PDF of the i th type of neighboring atom about each j th origin atom. The PPDFs give much more detailed information about the structure and are preferred when available. The most common samples studied by diffuse elastic scattering are either liquids, amorphous solids or polycrystals. In this case, the PDF (PPDF) is averaged over angle and gives the probability that a pair of particles is a distance R apart at the same time, and is called the (partial) radial distribution, correlation, or density function.

The PDF or local structure determines the actual distance between atoms while, when local disorder is present, the diffraction structure does not correctly display the actual distances between atoms. For any fundamental understanding of the properties of materials, a knowledge of the actual distances between atoms is important, since the atom-atom interaction is a strong function of this distance.

In the cases discussed here the PPDFs were determined by the X-ray absorption fine structure (XAFS) technique which in its range to about the fourth nearest neighbor has a decided advantage over other techniques in determining the PPDF, especially for dilute probe atoms [11]. For the La_2CuO_4 -based superconductors which are layered structures it is possible to obtain X-ray polarization-dependent PPDF informa-

tion about the c -axis for samples which are single crystals. Our XAFS measurements were performed on samples of aligned single crystal grains which can be optimized for obtaining the best signal. Such measurements are essential for the La_2CuO_4 -based superconductors as it allows the separation of neighboring atoms of the same type that have overlapping distances but make different angles with the c -axis, as is the case for the neighboring O(1) and O(2) oxygen atoms (in the Cu—O₂ and La—O planes, respectively) about the La and Cu sites [2,4–7]. Such separation is not unambiguously possible for disoriented powders. The knowledge gained by distinguishing the oxygens allows the determination of the rotation angle of the Cu—O₆ octahedra in the La_2CuO_4 -based high- T_c s, which identifies the various crystal structures that occur as a function of both temperature and composition. In addition, a unique feature of XAFS allows the direct determination of three body correlations to give $\langle \beta^2 \rangle$ where the angular brackets are an average over the sample and β is the buckling angle in the Cu—O₂ planes. Figure 1 shows the crystal structure of La_2CuO_4 in its high-temperature tetragonal phase (HTT), where the axes of the Cu—O₆ octahedra are parallel to the c -axis.

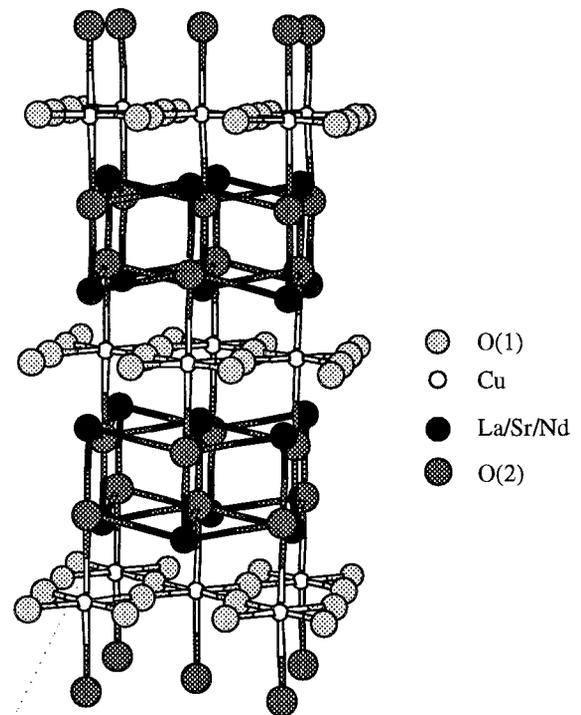


Fig. 1. The HTT phase of La_2CuO_4 .

3. ORIENTATION DEVIATIONS FROM PERIODICITY

There are two types of nanostructure deviations from periodicity found in the La_2CuO_4 -based superconductors. One is the expected induced localized displacement of the alloying, dopant and their neighboring atoms from periodic lattice sites. The other is a more unexpected deviation of orientation disorder. We present only the latter in this paper since some of them are dynamic.

3.1. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

We have studied [2,4] this material with XAFS for the Sr dopant range $0.02 \leq x \leq 0.36$. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ has two diffraction structures as a function of concentration x and temperature T . At low x and T , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is in the low temperature orthorhombic (LTO1) phase, while at high T for all x , and also at high x for all T , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is in the HTT phase. The difference between these two phases is illustrated in Fig. 2 which shows an O(2) oxygen surrounded by its nearest neighbor La atoms in the La—O(2) plane. Each O(2) is an apex atom to a Cu—O₆ octahedron. As the octahedra rotate about the a -axis passing through the center Cu atom to produce the LTO1 phase, the apex oxygen moves along the b -direction in the La—O(2) plane relative to its La neighbors.

In contrast, the local structure remains LTO1 over the same range. Changes in the local LTO1 structure do occur because of the magnitude of the

octahedra tilt angle to the c -axis decreasing to about half its value at $x \approx 0.15$ and then remaining constant up to the maximum concentration that was measured ($x = 0.36$). On the other hand, there is no detectable change in the local structure as a function of T up to room temperature. This contrast in the behavior of the local and diffraction structures indicates orientation disorder is present as discussed in Section 4.

3.2. $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$

Although Sr and Ba doping in La_2CuO_4 are commonly thought as equivalent, they are in fact very different. Ba doping brings about a different structural ground state in the SC region of the phase diagram, the LTT phase, in which Cu—O₆ octahedra are rotated about $\langle 110 \rangle$ -type axes, instead of the $\langle 100 \rangle$ tilts of the LTO phase (see Fig. 2). It is known that this new structure couples strongly to the hole carriers at $x \approx 0.125$, with the strength of the coupling regulated by the magnitude of the square of the tilt angle of Cu—O₆ octahedra for the small angles found in this material [12]. This coupling is manifested as an upturn of the resistivity below about 60 K, the temperature at which the LTT phase is stabilized, together with a strong T_c suppression [13]. It has also been clear for some time that the LTT phase bears a large amount of intrinsic disorder, as evidenced in the very broad diffraction peaks and large “thermal” ellipsoids [14], although a microscopic picture for the origin of such disorder was not clear. Our measurements at all La, Cu, and Ba sites of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ shed light onto the nature and origin of such disorder [5].

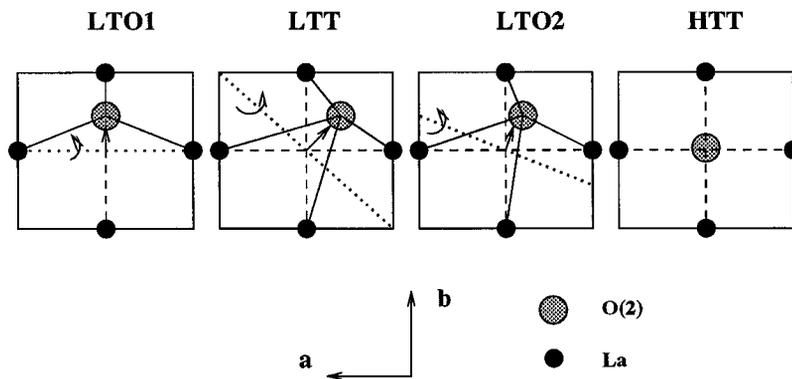


Fig. 2. La—O(2) displacements for Cu—O₆ octahedra tilts for (left to right) LTO1 ($Bmab$), LTT ($P4_2/ncm$), LTO2 ($Pccn$), HTT ($I4/mmm$). The oxygen atoms are the apical oxygens of the octahedra centered about Cu in the CuO₂-neighboring plane. Smaller correlated La displacements are neglected. The dotted lines are the projection of the axes of rotation in the Cu—O₂ plane that pass through the center of the neighboring Cu—O₆ octahedron. The a - and b -axes are those of the LTO1 structure.

As shown in Fig. 2 the splitting of La—O(2) planar distances is a measure of the tilt angle β which causes the same buckling angle β in the Cu—O₂ planes. We determined that the vast majority ($\geq 95\%$) of local tilts are LTT like, with a local tilt angle, averaged over all La sites, of $\langle\beta\rangle = 3.3(4)^\circ$, in good agreement with the $3.1(3)^\circ$ value of diffraction [5]. This average, local, tilt angle is determined from the average displacement of the distribution of the O(2) atoms from their location in the HTT phase. The mean square (σ_β^2) of the distribution about its average, however, is a measure of the local fluctuations in tilt angle. That this fluctuation is above what is expected from thermal disorder is easily seen from the much larger diffraction “thermal” ellipsoids (by about a factor of 2) obtained for distances involving O(2) atoms than those obtained for the same distances in the Sr-doped case [5]. We directly determined $\langle\beta^2\rangle$ from the XAFS signal of La—O(2)—Cu, Cu—O(2)—La/Ba, and Cu—O(1)—Cu nearly collinear multiple scattering (MS) paths which contain three-atom correlations [5].

Letting $\beta = \langle\beta\rangle + \delta\beta$ it follows that XAFS can determine the second moment of the local tilt angle distribution, $\sigma_\beta^2 = \langle\delta\beta^2\rangle = \langle(\beta - \langle\beta\rangle)^2\rangle = \langle\beta^2\rangle - \langle\beta\rangle^2$ since the local first moment $\langle\beta\rangle$ is known. A large disorder in β occurs with $\sigma_\beta \approx 2\langle\beta\rangle$ [5]. Furthermore, it is found that, on the average, the octahedra remain rigid during their orientation disordering.

La *K*-edge measurements on La_{2-x}Ba_xCuO₄, $x = 0.125, 0.15$, show that the local structure remains constant at LTT as T increases through the LTT \rightarrow LTO \rightarrow HHT phase transitions. This is consistent with previous findings by PDF analysis of neutron-scattering data on La_{2-x}Ba_xCuO₄ [15], which can detect the local structure out to larger dimensions, and gives an estimate that the correlation length of the LTT regions is ≈ 1 nm.

3.3. La_{1.6-x}Sr_xNd_{0.4}CuO₄

This material is of special interest because of the discovery of static stripes in the low temperature $x = 0.12$ phase by neutron diffraction [16]. Samples with $x = 0.12, 0.16$ were measured [7], corresponding to the dip and maximum in T_c . The local structure for $x = 0.12$ does not correspond to any of the *average* periodic structures determined for this material by diffraction. The Cu—O₆ octahedra are found to tilt $4.6 \pm 0.4^\circ$ from the *c*-axis along an axis in the *a*-*b* plane $20.4 \pm 5^\circ$ from the *a*-axis. This suggests the LTO2

structure, though the octahedra become somewhat distorted and the more distant atoms do not fit the LTO2 structure. In contrast, the local structure of $x = 0.16$ does fit the LTO2 structure and has corresponding tilt values of $3.8 \pm 0.5^\circ$ and $19.5 \pm 7.5^\circ$. The local structures for both concentrations are found to be independent of temperature, indicating that the various crystal phase transitions found in diffraction (HTT, LTO1, and LTT) are all due to long-range averaging of local structure regions with orientation disorder as discussed in Section. 4. Similar to La_{2-x}Ba_xCuO₄ large amount of disorder occurs in the magnitude of the local tilt, and thus buckling angles in the Cu—O₂ planes, with $\sigma_\beta \approx 2\langle\beta\rangle$ for both values of x .

4. DISCUSSION AND SUMMARY

All of the La₂CuO₄-based materials have orientation disorders of their Cu—O₆ octahedra which can be understood by referring to Fig. 2. La_{2-x}Sr_xCuO₄ is discussed first as its diffraction and local structures have been most extensively investigated as functions of x and temperature T . The local and diffraction structures are the same at low T in La_{2-x}Sr_xCuO₄ up to $x \approx 0.15$ but differ as T and x increase above these values, indicating the presence of orientation disorder. In addition, when the diffraction structure at low T transforms from LTO1 to HTT at $x = 0.20$ there is no detectable effect on T_c vs. x . This latter behavior is consistent with our conclusion that the local structure determines T_c behavior, and not the diffraction structure.

To appreciate the type of orientation disorder present in La_{2-x}Sr_xCuO₄ consider the difference between the HTT and LTO1 structures. The structural unit to consider is the Cu—O₆ octahedron. In HTT this unit has zero tilt to the *c*-axis while in LTO1 the tilt appears as an antiferrodistortive rotation about an axis parallel to the *a*-axis (Fig. 2) with the rotation alternating from positive to negative from neighbor to neighbor along the *b*-axis, doubling the unit cell in that direction. For $0.15 \leq x \leq 0.20$ where both diffraction and local structures are LTO1 but the tilt angle of the diffraction structure is becoming monotonically smaller with increasing x at low temperature while the local structure maintains a constant tilt angle, a growing fraction of local tilts are becoming orientation disordered and average to zero. This fraction reaches one at the second-order phase transition. At fixed x a partial disordering of the tilt angle occurs as T increases

and again the LTO1 to HTT second order transition occurs as the fraction of disorder reaches one.

In a similar manner the various differences between the local and diffraction structures that occur in $\text{La}_{1.6-x}\text{Sr}_x\text{Nd}_{0.4}\text{CuO}_4$ can be explained by disordering of the octahedra tilt directions. At low temperatures and for the measured concentrations $x = 0.12, 0.16$, the local structure for fixed x remains LTO2 with constant tilt angle up to room temperature, the highest measured. However, the magnitude of octahedral tilt angle decreases from $x = 0.12$ to $x = 0.16$. The various phases that occur by diffraction can be understood by referring to Fig. 2. The disordering of the tilt angle producing LTT from LTO2 can be accomplished by the O(2) apical oxygen atoms of the $\text{Cu}-\text{O}_6$ octahedra equally populating the equal energy sites obtained by reflection about the diagonal of the LTO2 square in Fig. 2. Similarly, the LTO1 average phase is produced by also equally populating the sites related by symmetry of reflection about the b -axis in LTT. Finally, the HTT phase can be obtained at high temperatures by also populating the sites related by symmetry of reflection about the a -axis in LTO1 (Fig. 2).

In $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ the LTO1 and HTT higher temperature diffraction phases are obtained from the temperature independent LTT local structure by the same disordering of octahedral tilts as described for $\text{La}_{1.6-x}\text{Sr}_x\text{Nd}_{0.4}\text{CuO}_4$.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ has insignificant buckling disorder in the $\text{Cu}-\text{O}_2$ plane and the largest value of $T_c \approx 40$ K, while both $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{La}_{1.6-x}\text{Sr}_x\text{Nd}_{0.4}\text{CuO}_4$ have large buckling disorder (larger than the average buckling angle) and lower $T_c \approx 30$ K, 20 K, respectively. This suggests that disorder in the buckling angle is detrimental to T_c . Since at low temperature the LTT phase of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ has no dynamic tilt disorder, yet has a large buckling disorder coming from the static displacements induced by doping the La-sites with the larger Ba atoms [5], all of its buckling is static. Any dynamic portion of the buckling comes from the disordering of regions of nanometer scale which appear to be greater than the coherence length of high- T_c . Within this scale the tilts are not disordered and thus the dynamic tilt disordering is not expected to affect T_c . It also follows that the local structure is the relevant one when considering the pairing mechanism for the materials investigated here, consistent with the behavior of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The static buckling induced by the substitution of foreign atoms which introduce disorder within a superconducting coherence length are the cause of the deterioration of high- T_c .

The substitution of foreign atoms in the La_2CuO_4 -based superconductors produces distortions both in the $\text{Cu}-\text{O}_2$ and $\text{La}-\text{O}$ planes. Since substitution of foreign atoms in the $\text{Cu}-\text{O}_2$ planes is much more detrimental to T_c than in the $\text{La}-\text{O}$ planes [17], as expected since the carriers are concentrated there, it is reasonable to assume that disorder in the CuO_2 planes would be the dominant contributor to the deterioration of T_c .

In summary, our results are consistent with a model that the local, not the diffraction structure, determines high- T_c in the La_2CuO_4 -based materials. Dynamical orientation disorder of the tilts of $\text{Cu}-\text{O}_6$ octahedra do not affect T_c because the correlation lengths of the tilts are larger the SC coherence lengths. Only disorder on a scale less than the coherence length will affect T_c in a detrimental fashion and this occurs by static-buckling disorder on the $\text{Cu}-\text{O}_2$ planes (where the carriers are concentrated) induced by the introduction of foreign atoms that substitute for the La atoms in the La_2CuO_4 -based materials. Foreign atoms that sit on the $\text{Cu}-\text{O}_2$ planes are even more detrimental to T_c , such as Ni and Zn, i.e., more disorder, more detriment—but details of the perturbed regions are important for a quantitative understanding [8].

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